

Search for high- T_C conventional superconductivity at megabar pressures in the lithium-sulfur system

Christian Kokail,¹ Christoph Heil,² and Lilia Boeri¹

¹*Institute of Theoretical and Computational Physics, Graz University of Technology, NAWI Graz, 8010 Graz, Austria*

²*Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom*

(Dated: May 25, 2016)

Motivated by the recent report of superconductivity above 200 K in ultra-dense hydrogen sulfide, we search for high- T_C conventional superconductivity in the phase diagram of the binary Li-S system, using *ab-initio* methods for crystal structure prediction and linear response calculations for the electron-phonon coupling. We find that at pressures higher than 20 GPa, several new compositions, besides the known Li_2S , are stabilized; many exhibit electride-like *interstitial* charge localization observed in other alkali metal compounds. Of all predicted phases, only Li_3S at $P > 640$ GPa displays a sizable T_C , in contrast to what is observed in sulfur and phosphorus hydrides, where several stoichiometries lead to high T_C . We attribute this difference to $2s$ - $2p$ hybridization and avoided core overlap, and predict similar behavior for other alkali metal compounds.

PACS numbers:

The successful prediction of a record critical temperature (T_C) of 203 K in hydrogen sulfide (H_3S) at 200 GPa [1–3] gave a considerable impulse to the *ab-initio* design of new high- T_C superconductors at extreme pressures. H_3S was in fact the first example of a *conventional* high-temperature superconductor whose crystal structure and T_C were first predicted completely from first-principles, and later confirmed experimentally. It is now understood that its record-high T_C stems from the constructive interference of large vibrational frequencies, electronic van-Hove singularities at the Fermi level and large electron-phonon (ep) matrix elements due the formation of *covalent* H-S bonds. [3–11] A few months after H_3S , a high- T_C superconducting phase was also found in compressed phosphines, which is compatible with several *metastable* PH_x phases identified by first-principles calculations. [12–15] Recent reports of metallization in hydrogen at ~ 350 GPa have risen the hope to attain superconductivity at room temperatures, or even higher. [16–22] While several hydrides have been proposed as prospective superconductors along the lines of H_3S ; [23–28] high- T_C superconductivity at high pressures in hydrogen-free compounds is still a largely unexplored field.

In this work we search for high- T_C superconductivity at extreme pressures in the Li-S system, using the USPEX method for *ab-initio* evolutionary crystal structure prediction, [29] and density functional perturbation theory (DFPT) calculations of the ep coupling as implemented in QUANTUM ESPRESSO. [30, 31] The underlying idea is to explore a hydrogen-free system similar to H_3S ; Li-S is a natural choice, because lithium belongs to the same group as hydrogen (similar chemical properties) and has a small atomic mass (large phonon frequencies). At ambient pressure, Li-S is stable in crystalline form in the Li_2S composition; this compound has applications in lithium-based batteries, and has been investigated by several authors. [32, 33] We find that at

high pressures several new phases are stabilized, many of which behave quite differently from the corresponding hydrides; in particular, superconductivity is harder to attain, and the typical T_C 's are much lower. We will show that this can be explained by the different chemistry of the two elements, caused by the presence or absence of core electrons. [34]

In fact, lithium passes through a sequence of transitions under pressure from close-packed, metallic structures to open, semi-metallic or semiconducting ones. [35–38] The increasing covalency is induced by the growing $2s$ - $2p$ hybridization, and is accompanied by the characteristic phenomenon of *interstitial charge localization*, i.e. the electronic valence charge tends to localize in interstitial regions of the crystal to minimize the overlap with underlying atomic core states (*avoided core overlap*). [39–43] Hydrogen, whose $1s$ valence electrons have no underlying core and are well separated in energy from $2p$ states, has a completely different behavior, transforming from molecular, insulating to close-packed metallic structures at very high pressures. [44] The highest T_C 's in the two elements range from ~ 16 K, measured in lithium at 100 GPa, [45, 46] to ~ 350 K predicted for hydrogen in the metallic phase. [16–19]

Figure 1 shows our theoretical phase diagram for the Li-S system, constructed with a four-step procedure. (i) First, we performed a preliminary scan of the phase space, with variable-compositions evolutionary algorithm (EA) runs from 0 to 600 GPa at 50 GPa intervals. (ii) For the most promising phases, i.e. those which lie on the convex hull, we ran additional calculations at fixed compositions with 100 GPa intervals starting from 0 GPa to identify thermodynamically stable phases. (iii) The best three structures from each fixed composition run were relaxed once more with stricter convergence parameters, to ensure the correct enthalpy hierarchy of the phases. (iv) The best individuals were relaxed further with a

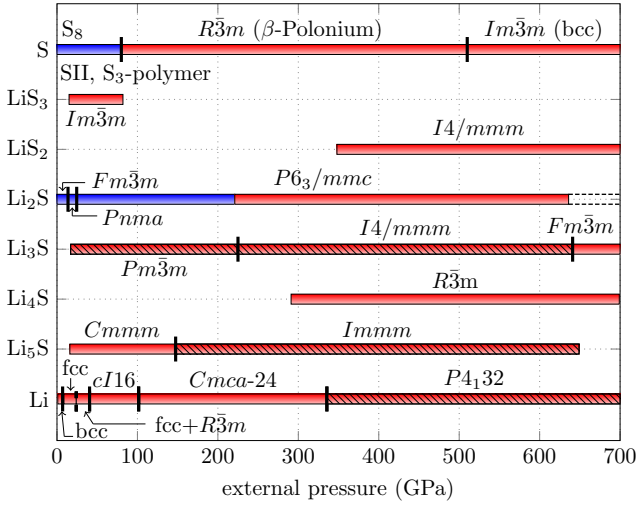


Figure 1. (Color online) Phase diagram for the Li-S system predicted by our DFT-EA search. The vertical bars delimit regions of stability. Blue and red bars indicate insulating and metallic phases, respectively. Shaded areas indicate phases with interstitial charge localization (*see text*).

tighter convergence threshold, at pressure intervals of 50-100 GPa, and the resulting energy vs. volume curves were then fitted to a Murnaghan equation of state. [47] This allowed us to obtain analytical expressions for the enthalpy vs. pressure relation for all structures, from which we could extract accurate stability ranges for all phases. [48, 49] Note that, in order to maintain our search within a reasonable time limit, we restricted the search space to phases with a maximum of 24 atoms per unit cell and 6 atoms per formula unit (*f.u.*).

Before discussing the new phases found in our EA search, we note that our calculations reproduce accurately literature results for the known phases, that is, for the two end members and Li_2S . For elemental lithium, we find essentially the same phase diagram as Ref. 50, i.e. we predict a transition from a *bcc* to a *fcc* phase and then into a *cI16* phase, stable until 100 GPa. [35] At 100 GPa, a *Cmca* phase with 24 atoms is stabilized, and remains the lowest in enthalpy up to ~ 330 GPa, where a simple cubic (*P4₁32*) phase occurs. Our results are in very good agreement with previous works which employ unit cells up to 24 atoms, [36, 37] while recent calculations with larger supercells predicted two additional phases between 60 and 270 GPa – *Aba2*-40 (40 atoms per cell) and *Cmca*-56 (56 atoms per cell). Having verified that the enthalpy differences with respect to the *Cmca*-24 phases are minimal and do not affect the calculated convex hull, we decided to use the *Cmca*-24 phase in the whole range. For sulfur, we predict a transition from the S_8 α phase to the polymeric S-II (2 GPa) and S_3 -polymer (20 GPa) phases. [51] At 80 GPa, the S_3 -polymer phase transforms into the β -Po phase, which is metallic. At

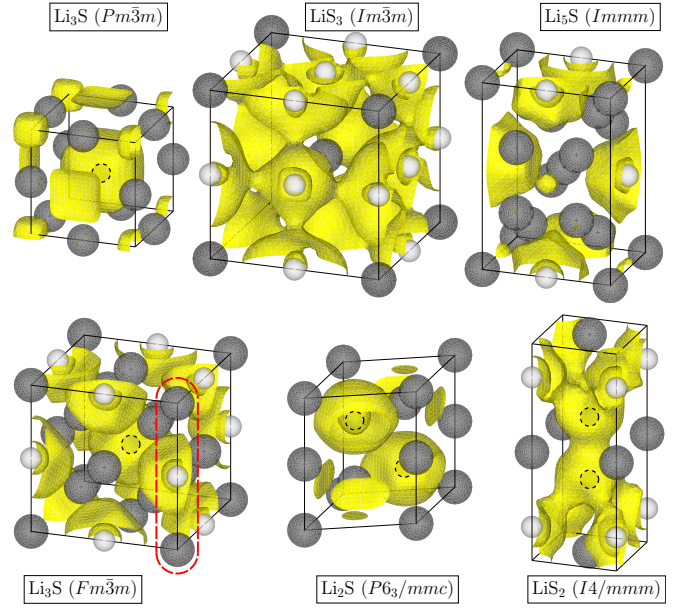


Figure 2. (Color online): Crystal structure and isocontour (0.65) of the ELF for (top): Li_3S - *Pm3m* (100 GPa), LiS_3 - *Im3m* (100 GPa), Li_5S - *Immm* (500 GPa), (bottom) Li_3S - *Fm3m* (500 GPa), Li_2S - *P6₃/mmc* (500 GPa) and LiS_2 - *I4/mmm* (500 GPa). The structures are shown in scale; Li and S atoms are shown as black and white spheres, respectively. Black, dashed circles indicate the location of S hidden by isosurfaces; red, dashed lines indicate important bonds (*see text*).

very large pressures (~ 510 GPa) we predict a transition to a standard *bcc* phase, as in Ref. 52. In agreement with previous calculations, and despite several attempts, we did not find any indication of a *bco* phase as seen by experiments between 83 and 162 GPa. [53] For Li_2S , we correctly predict a transition from the antifluorite structure (*Fm3m*) at ambient pressure to the anticuntunite structure at 13 GPa. At pressures higher than 26 GPa, a Ni_2In -type structure (*P6₃/mmc*), shown in Fig. 2, becomes stable; similar transition sequences are observed in other alkali-metal sulfides as Na_2S and K_2S , [54, 55] as well as in the closely related compound Li_2O . [33] The *P6₃/mmc* phase remains insulating up to 221 GPa, where an insulator-to-metal transition takes place; we find that this phase remains stable up to the highest pressure we calculated.

For pressures higher than 20 GPa, several new compositions are stabilized; the relative structures are detailed in the supplementary material (SM), [56] together with band structure plots and results of DFPT calculations. Figure 2 only shows those relevant to our discussion, decorated with isosurfaces of the electronic localization function (ELF). We start the discussion from the Li-rich side: The Li_5S composition becomes stable at 15 GPa, in an orthorhombic *Cmcm* structure, with 12 atoms in the unit cell. This is a very open and weakly metallic structure.

At ~ 130 GPa, Li_5S transforms to a more densely packed $Immm$ phase, shown in the first row of Fig. 2. The new phase shows signatures of interstitial charge localization around the center of the tetragonal faces. The Li_4S stoichiometry is stabilized only at extreme pressures ($P > 290$ GPa); the lowest-enthalpy structure is trigonal, with 10 atoms in the unit cell. Due to the low symmetry and poorly metallic behavior, we do not investigate this structure any further, but keep it in the convex hull because it has a strong influence on the stability of other phases.

Li_3S is of particular interest, as it has the same stoichiometry as high- T_C H_3S . Its stability ranges from 20 GPa up to the highest pressure investigated. The lowest-enthalpy structure at 20 GPa, shown in the top left corner of Fig. 2, has $Pm\bar{3}m$ space group. Sulfur occupies the $1b$ positions at the center of the cube, and lithium the $3d$ positions at the middle of the edges. Around the cube corners, there are large regions of empty space; the ELF isocontours show that a substantial fraction of charge tends to localize in these regions. Above 220 GPa, the simple cubic structure is destabilized towards an $I4/mmm$ variant, with three *f.u.* in the unit cell, in which three cubic cells are stacked along one of the cubic axes, with a small in-plane mismatch. Except for the different stacking, the interatomic distances and interstitial charge localization are very similar to the $Pm\bar{3}m$ phase. At 640 GPa, the simple cubic arrangement is finally destabilized towards a completely different phase, with space group $Fm\bar{3}m$, shown in the bottom left corner of Fig. 2. This structure, which has been reported at high pressures for Li_3N [57] is very closely packed. In this case, the ELF shows that the valence charge, which can no longer occupy the interstitial regions rearranges and Li forms strong bonds with its second nearest neighbor S along the (100) direction, indicated by the red, dashed line in Fig. 2. As we will show in the following, the suppression of interstitial charge localization in $Fm\bar{3}m$ - Li_3S is the reason this structure is the only high- T_C superconducting phase of our study. The two S-rich phases (LiS_2 and LiS_3) have very different structures and stability ranges. LiS_3 crystallizes in the same $Im\bar{3}m$ structure as H_3S , with S occupying the $6b$ Wyckoff positions of hydrogen, and Li the $2a$ of S; this phase, shown in the middle of the first row in Fig. 2, is thermodynamically stable only between 20 and 80 GPa. LiS_2 crystallizes in an $I4/mmm$ crystal structure, with two *f.u.* – middle of lower row in Fig. 2 – which is metallic and lies on the convex hull at pressures larger than 350 GPa. Both phases are superconducting with moderate T_C 's.

Our precedent study shows that there are fundamentally three pressure regimes in the high-pressure phase diagram of the Li-S system in Fig. 1: (a) a low-pressure regime ($P < 15$ GPa), where Li_2S is the only stable composition; (b) an intermediate regime ($P < 200$ GPa), where new stoichiometries are stabilized; some of the new phases, such as LiS_3 , disappear at higher pressures, while

others remain; and (c) a high-pressure regime, where new phases appear again. With the exception of Li_2S below 221 GPa, we identified all new phases as metallic, which leaves us with an extremely large pool of potential high- T_C conventional superconductors.

For a given crystal structure and chemical composition, the superconducting T_C due to *ep* interaction can be estimated through the Mc-Millan-Allen-Dynes formula:

$$T_c = \frac{\omega_{\log}}{1.2k_B} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]. \quad (1)$$

Here, k_B is the Boltzmann constant and μ^* is the Coulomb pseudopotential. The *ep* coupling constant λ and the logarithmic average phonon frequency ω_{\log} are obtained from the Eliashberg spectral function for the *ep* interaction $\alpha^2F(\omega)$, calculated within DFPT: [30]

$$\alpha^2F(\omega) = \frac{1}{N(E_F)} \sum_{\mathbf{k}\mathbf{q},\nu} |g_{\mathbf{k},\mathbf{k}+\mathbf{q},\nu}|^2 \delta(\epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{k}+\mathbf{q}}) \delta(\omega - \omega_{\mathbf{q},\nu}), \quad (2)$$

as: $\lambda = 2 \int d\omega \frac{\alpha^2F(\omega)}{\omega}$; $\omega_{\log} = \exp \left[\frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2F(\omega) \ln(\omega) \right]$. In Eq. 2, $N(E_F)$ is the density of states (DOS) at the Fermi level, $\omega_{\mathbf{q},\nu}$ is the phonon frequency of mode ν and wavevector \mathbf{q} and $|g_{\mathbf{k},\mathbf{k}+\mathbf{q},\nu}|$ is the electron-phonon matrix element between two electronic states with momenta \mathbf{k} and $\mathbf{k} + \mathbf{q}$ at the Fermi level. [58, 59]

Since *ep* coupling calculations in DFPT are computationally much more demanding than electronic structure calculations, we could not afford a full scan of the phase space at all pressures and compositions. Instead, we selected two pressures, 100 and 500 GPa, representative of the intermediate and high-pressure regimes respectively, and performed T_C calculations for all phases which are stable at these pressures or in their immediate vicinity.

The calculated values of T_C are plotted in Fig. 3, as green (100 GPa) and red (500 GPa) symbols. Literature values for different sulfur hydrides from Ref. [60] are shown as blue symbols on the same scale; the error bars indicate pressure variations of T_C , when known. To give a visual impression of the presence or absence of superconductivity, T_C 's smaller than 0.5 K are shown as negative. Table I reports the corresponding values of ω_{\log} and λ . Since we could not find any literature values, we calculated also data for the $P4_132$ phase of Li at 500 GPa.

Figure 3 shows that only a few Li-S phases display a finite T_C , and a single phase – i.e. the high-pressure *fcc* phase of Li_3S – displays a critical temperature comparable to that of hydrides. Furthermore, two of the phases with a finite T_C , LiS_3 and LiS_2 , are S-rich phases, in which the *ep* coupling is dominated by the sulfur sublattice, and thus not directly related to hydrides. Other Li-rich phases, including elemental Li, exhibit T_C 's lower than 20 K. The contrast with the corresponding hydrides is striking: for some compositions the differences in T_C

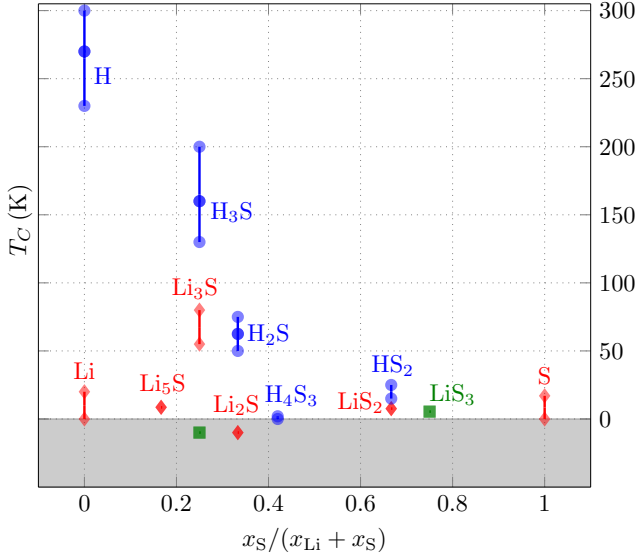


Figure 3. (Color online) Calculated T_C 's of intermediate (green) and high (red) pressure Li-S phases. Blue symbols indicate values for the H-S system, taken from literature. [60, 61] The error bars show the variations of T_C due to pressure, when available. Phases with no superconductivity are shown as negative values.

are as large as two orders of magnitude. This suggests a fundamental difference between hydrogen- and lithium-rich compounds that we will investigate based on Eq. 1 and Tab. I.

First, the higher atomic mass of lithium implies a smaller prefactor ω_{\log} in Eq. 1: to a first approximation, the reduction can be estimated as: $\sqrt{M_{Li}/M_H} \simeq 2.6$. For most cases reported in Tab. I, this is clearly not the dominating effect. The single notable exception is $Fm\bar{3}m$ -Li₃S, which is the only truly high- T_C phase identified in our study - its T_C is 80 K at 500 GPa, and decreases to 55 K in its stability range. If we take into account the mass effect, the T_C is comparable to that of H₃S. To prove that, we performed a calculation in which we replaced the Li mass with that of hydrogen; this phase is indicated as Li₃S^H in the table. The calculated T_C is 170 K, i.e., comparable to that of H₃S. We want to note, however, that the pressure needed to stabilize a high- T_C phase in this case is almost three times larger as in the hydrides. We will discuss this point further in the following.

Table I shows that, with the exception of $Fm\bar{3}m$ -Li₃S, where $\lambda \geq 1$, all Li-S phases have small, or at best intermediate ep coupling constants ($0.1 < \lambda < 0.55$). The simplified Hopfield expression: $\lambda = \frac{N(E_F)I^2}{M\omega^2}$, where I is an average ep matrix element and $M\omega^2$ is an average lattice force constant permits to separate the ep coupling into a purely electronic contribution given by the DOS and a factor $\eta = \frac{I^2}{M\omega^2}$, related to the lattice. Values of

Table I. Superconducting properties of the metallic Li-S phases. T_C 's are estimated from Eq. 1, with $\mu^*=0.1$. Pressures are in GPa, ω_{\log} and T_C 's are in K; $\tilde{N}(E_F)$ is the DOS at the Fermi level, in st/Ry, divided by the number of atoms in the unit cell; $\eta = \lambda/\tilde{N}(E_F)$ is in Ry · atom. Data for H₃S are from Ref. 6.

comp.	P	ω_{\log}	λ	T_C	$\tilde{N}(E_F)$	η
Li ₃ S ($Pm\bar{3}m$)	100	754	0.08	0.0	0.62	0.13
Li ₃ S ($Im\bar{3}m$)	100	409	0.52	5.4	1.45	0.36
Li ($P4_132$)	500	546	0.40	2.2	0.25	1.64
Li ₅ S ($Immm$)	500	420	0.53	8.6	0.48	1.10
Li ₃ S ($Pm\bar{3}m$)	500	702	0.25	0.0	0.67	0.37
Li ₃ S ($Fm\bar{3}m$)	500	773	1.43	80.0	1.67	0.85
Li ₃ S ($Fm\bar{3}m$)	600	826	1.01	55.9	1.30	0.78
Li ₂ S ($P6_3/mmc$)	500	374	0.22	0.0	0.27	0.85
Li ₂ S ($I4/mmm$)	500	494	0.54	7.6	1.35	0.40
H ₃ S ($Im\bar{3}m$)	200	1200	2.40	180	1.83	1.31
Li ₃ S ^H ($Fm\bar{3}m$)	500	1156	1.43	169	1.67	0.86

$\tilde{N}(E_F)$, i.e. DOS per atom, and η for all Li-S phases in Fig. 3 are reported in Tab. I.

First of all, we notice that in three high-pressure phases, simple cubic Li, Li₅S and Li₂S, λ is suppressed by an extremely low $\tilde{N}(E_F)$. For Li and Li₅S, the poor metallic behavior is a consequence of $2s$ - $2p$ hybridization; Li₂S is instead a semiconducting phase which has metalized by band overlap, and its DOS is intrinsically low. In the two sulfur-rich phases – LiS₂ and LiS₃ – the ep coupling is moderate ($\lambda \sim 0.55$) and the DOS is sizable; due to the high sulfur content the characteristic phonon frequencies and T_C 's are relatively low.

Interestingly, for Li₃S we observe a striking difference between the simple cubic (sc) $Pm\bar{3}m$ low-P and the fcc $Fm\bar{3}m$ high-P structures: The sc phase has an extremely low $\lambda = 0.08$ in its stability range, which increases slightly at 500 GPa ($\lambda = 0.25$), where it is still dynamically stable; both values yield negligible T_C 's. The high- T_C fcc phase, instead, exhibits a very high coupling ($\lambda = 1.43$) at 500 GPa and $\lambda = 1.01$ at higher pressures (600 GPa); the corresponding T_C 's are large.

Table I shows that in this case, besides the DOS, there is a remarkable difference in the lattice contribution to the ep coupling, η , between the low and high-pressure phases. This is due to the different nature of electronic states involved in the superconducting pairing in the two structures. In fact, the double- δ integral in Eq. 2 implies that the only electronic states, which give a finite contribution to the ep coupling are those that are at E_F . If these states have a large intrinsic coupling to

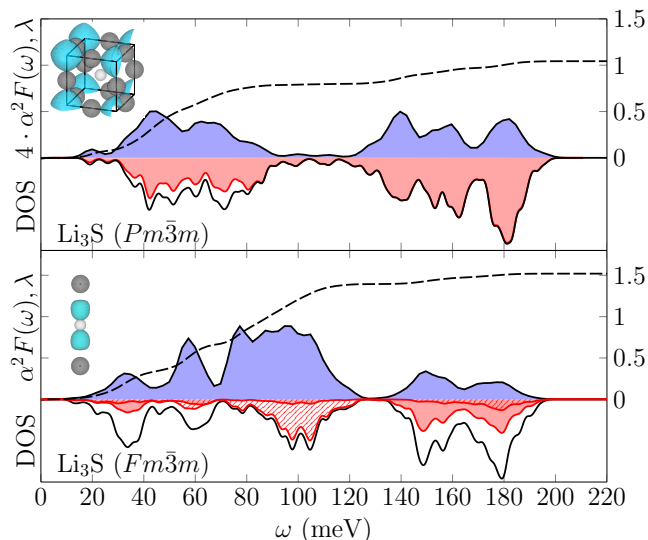


Figure 4. (Color online) Above: $\alpha^2 F(\omega)$ for $Pm\bar{3}m$ - Li_3S (top) and $Fm\bar{3}m$ - Li_3S (bottom) at 500 GPa; the black, dashed lines show the frequency-integrated ep coupling $\lambda(\omega)$. Note that the data for $Pm\bar{3}m$ - Li_3S are multiplied by four. Below: Phonon DOS's. Partial lithium contributions are shown in red; the dashed areas in $Fm\bar{3}m$ - Li_3S indicate vibrations of the Li atoms which form bonds with S in the (100) direction – red dashed lines in Fig. 2. The insets show isocontours of the square of the wavefunction for the electronic bands that cross the Fermi level.

phonons, as in covalently-bonded solids, η , and thus λ , are large. [4, 5, 62] On the contrary, interstitial electrons, which are localized in empty regions of the crystal structure, couple very little to lattice vibrations, and hence η and λ will be low.

Figure 4 illustrates how the superconducting properties of $Pm\bar{3}m$ - and $Fm\bar{3}m$ - Li_3S differ due to matrix elements effects. The two main panels show the Eliashberg spectral functions and partial phonon DOS's calculated for both phases at 500 GPa: the two spectra extend up to 180 meV, but the intensity and spectral distribution of the ep coupling is crucially different. Note that for better readability of the figure, $\alpha^2 F(\omega)$ and λ of $Pm\bar{3}m$ - Li_3S are multiplied by four. $Pm\bar{3}m$ - Li_3S has an extremely uniform (and low) ep coupling, while $Fm\bar{3}m$ - Li_3S shows a strong enhancement in the spectral region which corresponds to modes that distort the long Li-S bonds in the (100) direction. In the small insets we plot isocontours of the square of the wavefunctions for the electronic states at the Fermi level – see SM for the definition. [56] In $Pm\bar{3}m$ - Li_3S , these are localized in the interstitial region, i.e. around the corners of the cube. In $Fm\bar{3}m$ - Li_3S , on the other hand, they are localized along the edges of the cube, i.e. along the long (100) Li-S bonds, indicated by the red dashed lines in Fig. 2. The different nature of the electronic states leads to a factor of ~ 3 increase in η ; the difference in λ is even larger.

We thus find that interstitial charge localization due to avoided core overlap can be a fundamental limiting factor for conventional superconductivity. This feature is very common in many alkali-metal-rich phases, including several new Li-S phases of this study, indicated by dashed areas in in Fig. 1. When, as in $Pm\bar{3}m$ - Li_3S , the electron count is such that interstitial charge localization involve electrons at E_F , the ep coupling is strongly suppressed.

In conclusion, in this work we studied the thermodynamic stability and superconducting properties of the Li-S system up to 700 GPa, using methods for *ab-initio* crystal structure prediction and linear response calculations of the ep coupling. The calculated convex hulls show that several compositions besides the ambient pressure Li_2S are stabilized with increasing pressure. Most of these phases are metallic, but exhibit no or low- T_C superconductivity. We attribute this to two detrimental effects of core electrons in lithium: (i) an increased insulating behavior under pressure, due to hybridization between $2s$ and $2p$ electronic states; and (ii) interstitial charge localization due to avoided core overlap, which can bring states to the Fermi level that are intrinsically not coupled to lattice vibrations. This is observed for example in Li_3S , where a high- T_C (55-80 K) *fcc* phase appears only at pressures high enough to stabilize closed packed structures (> 600 GPa). Our study thus shows that high- T_C superconductivity at megabar pressures can be attained in Li-rich compounds, similarly to hydrides, but a general tendency to insulating behavior and avoided core overlap will limit the possible range of pressures and dopings.

The authors acknowledge computational resources from the *dCluster* of the Graz University of Technology and the VSC3 of the Vienna University of Technology.

-
- [1] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, *Nature* **000**, 2015/08/17/online (2015).
 - [2] I. Troyan, A. Gavriluk, R. Ruffer, A. Chumakov, A. Mironovich, I. Lyubutin, D. Perekalin, A. P. Drozdov, and M. I. Eremets, *Science* **351**, 1303 (2016), <http://science.sciencemag.org/content/351/6279/1303.full.pdf>.
 - [3] D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, *Sci. Rep.* **4** (2014), <http://dx.doi.org/10.1038/srep06968>.
 - [4] N. Bernstein, C. S. Hellberg, M. D. Johannes, I. I. Mazin, and M. J. Mehl, *Phys. Rev. B* **91**, 060511 (2015).
 - [5] C. Heil and L. Boeri, *Phys. Rev. B* **92**, 060508 (2015).
 - [6] Flores-Livas, José, Sanna, Antonio, and Gross, E. K.U., *Eur. Phys. J. B* **89**, 63 (2016).
 - [7] Y. Quan and W. E. Pickett, *Phys. Rev. B* **93**, 104526 (2016).
 - [8] Y. Li, J. Hao, H. Liu, Y. Li, and Y. Ma, *The Journal of Chemical Physics* **140**, (2014).
 - [9] D. A. Papaconstantopoulos, B. M. Klein, M. J. Mehl, and W. E. Pickett, *Phys. Rev. B* **91**, 184511 (2015).
 - [10] O. Luciano, E. Cappelluti, and L. Pietronero, (2015),

- arXiv: 1511.04304.
- [11] I. Errea, M. Calandra, C. J. Pickard, J. Nelson, R. J. Needs, Y. Li, H. Liu, Y. Zhang, Y. Ma, and F. Mauri, *Phys. Rev. Lett.* **114**, 157004 (2015).
 - [12] A. Drozdov, M. I. Erements, and I. A. Troyan, ArXiv e-prints (2015), [arXiv:1508.06224 \[cond-mat.supr-con\]](https://arxiv.org/abs/1508.06224).
 - [13] A. Shamp, T. Terpstra, T. Bi, Z. Falls, P. Avery, and E. Zurek, *Journal of the American Chemical Society* **138**, 1884 (2016), pMID: 26777416, <http://dx.doi.org/10.1021/jacs.5b10180>.
 - [14] J. A. Flores-Livas, M. Amsler, C. Heil, A. Sanna, L. Boeri, G. Profeta, C. Wolverton, S. Goedecker, and E. K. U. Gross, *Phys. Rev. B* **93**, 020508 (2016).
 - [15] Y. Fu, X. Du, L. Zhang, F. Peng, M. Zhang, C. J. Pickard, R. J. Needs, D. J. Singh, W. Zheng, and Y. Ma, *Chemistry of Materials* **28**, 1746 (2016), <http://dx.doi.org/10.1021/acs.chemmater.5b04638>.
 - [16] N. Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968).
 - [17] P. Cudazzo, G. Profeta, A. Sanna, A. Floris, A. Continenza, S. Massidda, and E. Gross, *Phys. Rev. Lett.* **100**, 257001 (2008).
 - [18] J. M. McMahon and D. M. Ceperley, *Phys. Rev. B* **84**, 144515 (2011).
 - [19] M. Borinaga, I. Errea, M. Calandra, F. Mauri, and A. Bergara, ArXiv e-prints (2016), [arXiv:1602.06877 \[cond-mat.supr-con\]](https://arxiv.org/abs/1602.06877).
 - [20] R. Szczeniński and M. Jarosik, *Solid State Communications* **149**, 2053 (2009).
 - [21] A. D. M. I. Erements, I. A. Troyan, ArXiv e-prints (2016), [arXiv:1601.04479 \[cond-mat.supr-con\]](https://arxiv.org/abs/1601.04479).
 - [22] E. G. Dalladay-Simpson, R. T. Howie, *Nature* **529**, 63 (2016).
 - [23] N. Ashcroft, *Phys. Rev. Lett.* **92**, 187002 (2004).
 - [24] J. S. Tse, Y. Yao, and K. Tanaka, *Phys. Rev. Lett.* **98**, 117004 (2007).
 - [25] G. Gao, A. R. Oganov, P. Li, Z. Li, H. Wang, T. Cui, Y. Ma, A. Bergara, A. O. Lyakhov, T. Iitaka, and G. Zou, *Proceedings of the National Academy of Sciences* **107**, 1317 (2010).
 - [26] D. Y. Kim, R. H. Scheicher, H.-k. Mao, T. W. Kang, and R. Ahuja, *PNAS* **107**, 2793 (2010).
 - [27] Y. Yao and D. D. Klug, *Proceedings of the National Academy of Sciences* **107**, 20893 (2010).
 - [28] J. A. Flores-Livas, M. Amsler, T. J. Lenosky, L. Lehtovaara, S. Botti, M. A. L. Marques, and S. Goedecker, *Phys. Rev. Lett.* **108**, 117004 (2012).
 - [29] A. Oganov, C. Glass, A. Lyakhov, H. Stokes, Q. Zhu, R. Agarwal, X. Dong, P. Perterra, Z. Raza, M. Salvado, *et al.*, .
 - [30] For selected phases we calculated the *ep* properties using DFPT, as implemented in QUANTUM ESPRESSO. [31]. We employed PBE ultrasoft pseudopotentials with semicore states in valence for lithium and sulfur from the standard QUANTUM ESPRESSO distribution, with energy cutoffs of 80 and 800 Ry for wavefunctions and charge density, respectively. We used 8^3 **k**- and **q**-points meshes for reciprocal space integration for electron and phonon states in the self-consistent calculations, and up to 38^3 **k**-points for the *ep* matrix elements.
 - [31] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *Journal of Physics: Condensed Matter* **21**, 395502 (19pp) (2009).
 - [32] A. Grzechnik, A. Vegas, K. Syassen, I. Loa, M. Hanfland, and M. Jansen, *Journal of Solid State Chemistry* **154**, 603 (2000).
 - [33] A. Lazicki, C.-S. Yoo, W. J. Evans, and W. E. Pickett, *Phys. Rev. B* **73**, 184120 (2006).
 - [34] I. I. Naumov, R. J. Hemley, R. Hoffmann, and N. Ashcroft, *The Journal of chemical physics* **143**, 064702 (2015).
 - [35] M. Hanfland, K. Syassen, N. Christensen, and D. Novikov, *Nature* **408**, 174 (2000).
 - [36] L. Shi and D. A. Papaconstantopoulos, *Physical Review B* **73**, 184516 (2006).
 - [37] N. Christensen and D. Novikov, *Physical Review B* **73**, 224508 (2006).
 - [38] M. Marqués, M. I. McMahon, E. Gregoryanz, M. Hanfland, C. L. Guillaume, C. J. Pickard, G. J. Ackland, and R. J. Nelmes, *Phys. Rev. Lett.* **106**, 095502 (2011).
 - [39] B. Rousseau and N. W. Ashcroft, *Phys. Rev. Lett.* **101**, 046407 (2008).
 - [40] M. Marqués, G. J. Ackland, L. F. Lundegaard, G. Stinton, R. J. Nelmes, M. I. McMahon, and J. Contreras-García, *Phys. Rev. Lett.* **103**, 115501 (2009).
 - [41] M. Gatti, I. V. Tokatly, and A. Rubio, *Phys. Rev. Lett.* **104**, 216404 (2010).
 - [42] M. Marqués, M. I. McMahon, E. Gregoryanz, M. Hanfland, C. L. Guillaume, C. J. Pickard, G. J. Ackland, and R. J. Nelmes, *Phys. Rev. Lett.* **106**, 095502 (2011).
 - [43] Y. Xie, A. R. Oganov, and Y. Ma, *Phys. Rev. Lett.* **104**, 177005 (2010).
 - [44] C. J. Pickard and R. J. Needs, *Nat Phys* **3**, 473 (2007).
 - [45] Y. Yao, J. Tse, K. Tanaka, F. Marsiglio, and Y. Ma, *Physical Review B* **79**, 054524 (2009).
 - [46] G. Profeta, C. Franchini, N. Lathiotakis, A. Floris, A. Sanna, M. A. L. Marques, M. Lüders, S. Massidda, E. K. U. Gross, and A. Continenza, *Phys. Rev. Lett.* **96**, 047003 (2006).
 - [47] F. Murnaghan, *Proceedings of the National Academy of Sciences* **30**, 244 (1944).
 - [48] We explored the Li-S system using the technique of *ab-initio* evolutionary crystal structure prediction as implemented in the USPEX-package. [63–65] The underlying structural relaxations were performed using the VASP code, [66, 67] within the generalized gradient approximation. [68] We used the all-electron projector-augmented wave method. [69, 70] To avoid core overlap at high pressures in Li, we treated the 1s and 2s electrons as valence. Individual structures generated by the evolutionary algorithms were relaxed with increasing precision in a 5-step procedure; the energies were finally recalculated with increasing convergence criteria to ensure a correct ranking of the structure.
 - [49] For all evolutionary runs, we limited trapping in local minima by repeating simulations at selected pressures and using the antiseeds-technique described in Ref. [29]. To ensure a reliable ranking of the structures, we performed extensive convergence checks of the total energy and forces with respect to cut-off energy and k-point resolution; for variable and fixed composition runs we used energy cut-offs up to 700 up to 800 eV, and a k-point res-

- olution of $0.06\,2\pi/\text{\AA}$ to obtain a first rough approximation of the enthalpies; for the final enthalpy vs. pressure curves, we increased these values up to 1100 to 1200 eV and Monkhorst-Pack k-point meshes for sampling the Brillouin-zone with resolution of $0.03\,2\pi/\text{\AA}$, which ensured a convergence of forces up to 1 meV/atom.
- [50] Y. Ma, A. R. Oganov, and Y. Xie, *Physical Review B* **78**, 014102 (2008).
 - [51] A. R. Oganov and C. W. Glass, *The Journal of Chemical Physics* **124**, 244704 (2006), <http://dx.doi.org/10.1063/1.2210932>.
 - [52] O. Zakharov and M. L. Cohen, *Physical Review B* **52**, 12572 (1995).
 - [53] O. Degtyareva, E. Gregoryanz, M. Somayazulu, H.-k. Mao, and R. J. Hemley, *Physical Review B* **71**, 214104 (2005).
 - [54] A. Vegas, A. Grzechnik, K. Syassen, I. Loa, M. Hanfland, and M. Jansen, *Acta Crystallographica Section B: Structural Science* **57**, 151 (2001).
 - [55] A. Vegas, A. Grzechnik, M. Hanfland, C. Mühle, and M. Jansen, *Solid state sciences* **4**, 1077 (2002).
 - [56] Supplementary Material for this article is available online under...
 - [57] A. Lazicki, B. Maddox, W. J. Evans, C.-S. Yoo, A. K. McMahan, W. E. Pickett, R. T. Scalettar, M. Y. Hu, and P. Chow, *Phys. Rev. Lett.* **95**, 165503 (2005).
 - [58] J. P. Carbotte, *Rev. Mod. Phys.* **62**, 1027 (1990).
 - [59] P. B. Allen and B. Mitrović, *Theory of Superconducting T_c*, Solid State Physics, Vol. 37 (Academic Press, 1983) pp. 1 – 92.
 - [60] Y. Li, L. Wang, H. Liu, Y. Zhang, J. Hao, C. J. Pickard, J. R. Nelson, R. J. Needs, W. Li, Y. Huang, I. Errea, M. Calandra, F. Mauri, and Y. Ma, *Phys. Rev. B* **93**, 020103 (2016).
 - [61] R. Akashi, W. Sano, R. Arita, and S. Tsuneyuki, ArXiv e-prints (2016), [arXiv:1512.06680](https://arxiv.org/abs/1512.06680) [cond-mat.supr-con].
 - [62] L. Boeri, J. Kortus, and O. K. Andersen, *Phys. Rev. Lett.* **93**, 237002 (2004).
 - [63] A. R. Oganov and C. W. Glass, *The Journal of chemical physics* **124**, 244704 (2006).
 - [64] A. O. Lyakhov, A. R. Oganov, H. T. Stokes, and Q. Zhu, *Computer Physics Communications* **184**, 1172 (2013).
 - [65] A. R. Oganov, A. O. Lyakhov, and M. Valle, *Accounts of chemical research* **44**, 227 (2011).
 - [66] G. Kresse and J. Hafner, *Physical Review B* **47**, 558 (1993).
 - [67] G. Kresse and J. Furthmüller, *Computational Materials Science* **6**, 15 (1996).
 - [68] J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical review letters* **77**, 3865 (1996).
 - [69] G. Kresse and D. Joubert, *Physical Review B* **59**, 1758 (1999).
 - [70] P. E. Blöchl, *Physical Review B* **50**, 17953 (1994).